

ation, yielding hydrogen and carbon together with small quantities of unsaturated hydrocarbons, notably acetylene. On the other hand, petroleum has been shown by the important researches of Mabery to contain a series of hydrocarbons which are usually characteristic of reactions at high temperatures. The fact that such hydrocarbons occur in petroleum, whether in small or large quantities, is of very great interest and should have due weight in the selection of any hypothesis proposed to account for its origin. At present this fact can hardly be considered to furnish evidence either for or against the views of Mendeléeff in regard to the origin of natural gas.

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## ON THE OCCURRENCE OF PETROLEUM IN THE CAVITIES OF FOSSILS.

BY FRANCIS C. PHILLIPS.

(*Read February 5, 1897.*)

In the study of geological facts bearing upon the history of petroleum, much interest has been aroused during recent times by the discovery of petroleum enclosures in the cavities of fossils in limestone rocks. Such occurrences, observed in many places, and in deposits of different geological age, from the Silurian onward, have been regarded as furnishing proof that the genesis of oil is to be attributed to chemical changes taking place in the tissues of the original organism of the fossil, and therefore as strengthening a commonly accepted belief that the hydrocarbons contained in the rocks have originated from animal remains stored in the sediments which afterwards became consolidated into rock.

The relationship suggested between the petroleum and the fossils is all the more interesting and important since the oil-bearing sand rocks of the Devonian age do not, as a rule, contain remains of animal life, and furnish no satisfactory clues as to the origin of oil and gas. As tending to confirm the evidence which such facts have been supposed to furnish, numerous instances have been cited where hydrocarbons are apparently produced from remains of more recent animal life, as in coral reefs and in the accumulations of organic remains buried under marine or fluvial sediments. In certain

districts local accumulations have apparently led to the formation of petroleum and natural gas, and where evidence of so direct a character is at hand it has been argued that chemical changes of similar kind have been concerned in the production of hydrocarbons upon a larger scale in the rocks. But the fact most suggestive of a genetic relationship between the hydrocarbons of the rocks and the tissues of animal bodies is found in the frequent association of petroleum and bitumen with fossil remains.

A remarkable instance of this kind has been discovered at Williamsville, Niagara county, N. Y., by Mr. F. K. Mixer, of Buffalo. Corals in large masses, constituting a reef of considerable proportions, have been exposed in a limestone quarry at this place. The structure of the coral is well preserved and its rounded forms are standing erect as they grew in the original reef. In many parts the cells contain petroleum in a somewhat thickened or dried condition and the walls of the fossil seem to be saturated with oil. In other parts of the reef the cells contain a black substance resembling pitch or asphaltum, the color of which gives great distinctness to the delicate white lace-like partitions separating the cells. The distribution of petroleum and solid bitumen throughout the coral is somewhat irregular.

In viewing this reef, as it stands exposed in the quarry, various questions suggest themselves as to the origin of the hydrocarbons. If these have resulted from the carbon and hydrogen of the bodies of the polyps, how has it occurred that the organic matters were converted into paraffins instead of undergoing the usual process of oxidation and decay? The growth of the reef was undoubtedly slow, as a portion only of the polyps could have been living at any given time, the greater number of the cells being empty, the quantity of animal matter available for petroleum production must always have been small as compared with the total extent of the reef, and being scattered among separate cells oxidation of the remains of the isolated polyps would have been more likely to occur than their accumulation in masses. There does not seem to be any reason in this case for supposing that the corals in their living state were buried under masses of sediment. On the contrary, the limestone extending around and above the corals indicates a period of quiet and clear water. It is, therefore, difficult to understand how the soft tissues of dead coral animals could have been protected against destructive oxidation.

Pieces of this fossil taken from the quarry are on examination readily seen to contain an amount of petroleum at least equal in bulk to the cells of the coral. The solid bitumen occurring in other parts suffices to nearly fill the cells. These facts would render it difficult to account for the hydrocarbons on the supposition that they are due to chemical changes occurring in the tissues of the original organisms.

Le Bel (*Notice sur les Gisements de pétrole à Pechelbronn*, Colmar, 1885, p. 4) has observed that fossils frequently contain in their cavities a quantity of petroleum greater than could be produced from the organic matter of the original animal, even supposing that this organic matter had been converted wholly into petroleum.

Fraas (Jaccard, *Le Pétrole*, 1895, p. 60), in describing the occurrence of petroleum in a coral reef in the Red Sea, refers to the fact that oil collects in parts of the reef growing in shallow clear water and states that this oil is so abundant that it has been carried by Bedouins to Suez, where in 1868 it had become an article of commerce. Fraas believes that the oil is being produced by the decomposition of the organisms of the coral.

If the source of this petroleum is correctly interpreted, its occurrence under such conditions can hardly be considered to represent an isolated case. The reactions which take place during the conversion of animal remains into petroleum must be typical of changes occurring elsewhere, and must result normally under given conditions as to temperature, pressure and oxidizing influences. Wherever the same conditions exist in other reefs they should give rise to a similar constant production of petroleum and we should be justified in speaking of a "petroleum fermentation" coordinate with other naturally occurring organic changes.

It seems doubtful whether this petroleum can have originated in the coral where it is found and it is improbable that such an occurrence can serve to explain the origin of hydrocarbons in the Silurian fossils. I have been unable to learn that petroleum is found in the reefs at Bermuda. Dr. W. H. Dall, of the Smithsonian Institution, informs me that no occurrence of petroleum has been reported in the reefs of the Florida coast. If in the case of the Silurian coral at Williamsville the process of conversion into hydrocarbons was rapidly completed after the destruction of the animals, the oil would have floated to the surface of the water and little

would be left to impregnate the calcareous skeleton. If, on the other hand, the process was continued until the organic matters were buried under deep sediments and exposure to oxidation had ceased, then more distinct signs of a deposit of sediment over the entire reef should be looked for.

The conditions for effective oxidation of organic matters are rendered more complete under water by the presence of bacteria, and these must have aided greatly in promoting the final change of the tissues of the dead coral animals into nitrates, ammonia, carbon dioxide and water. In stream beds and under sediments the products of the decay of animal matters are mainly gaseous, and the contents of the coral cells must have been almost wholly lost in volatile form before a process of change into petroleum could have been begun in the much diminished residue of the original organisms.

It is possible that the occurrence of petroleum in the cells of a modern coral reef may find an explanation in a phenomenon often observed in the case of natural gas. I have elsewhere (*Journal of the American Chemical Society*, 1895, p. 801) called attention to the fact that on stirring the gravel which lies at the bottom of many streams in western Pennsylvania, it is common to find that gas bubbles are disengaged, and that such an accumulation of gas may occur where the stream flows over sandstone, covered by gravel a few inches only in depth, and where the character of the gravel renders it unlikely that gas could have originated locally. In such cases it is probable that the occurrence of gaseous hydrocarbons is due to an escape to the surface from deep-lying rock strata.

Petroleum escaping from the interstices of a rock might accumulate in the cavities and cells of dead corals. A slow oozing of petroleum from the surface of the ground is a well-known phenomenon in various parts of the oil regions.

The occurrence of petroleum in cavities of fossils might be traced to a former condition of wide distribution of oil throughout the rock, that is, in a form in which it is known to be present in limestones and shales in many places. The gradual access of moisture to the pores of a rock so impregnated would tend to cause a slow displacement of the oil. Water, insufficient to appear in liquid form upon a surface of fracture, might still suffice, as it gradually saturated the rock under the influence of capillary attraction, or of pressure, to displace the oil and cause it to accumulate in liquid

form in the cavities of fossils or in other open spaces. Moisture in such quantity as is absorbed by many dense rocks would tend slowly to remove liquid hydrocarbons, just as it might drive them from the cells of vegetable tissue. The region of least resistance to the movement of the oil would be a cavity. The accumulation of oil in open spaces in fossils would thus result from its displacement from adjacent, or perhaps distant, parts of the rock by water, which would tend to produce a retreat of the oil. If thus impelled by the movement of moisture through the rock the oil would gradually assume the liquid form if it passed into a cavity. The cells of corals and other open spaces might thus become reservoirs capable of holding collectively considerable quantities of oil.

It is true that before the original sediment became hardened into rock, the proportion of water present must have been considerable. In accordance with a commonly accepted view the process of petroleum formation was not completed until long after the sediments with their enclosed organic matters had been consolidated. The oil would then have been expelled from the rock, little by little, as it was being gradually produced. In this case also the movement of the oil might have led to its being caught in liquid form in cavities, or if it oozed out at the surface of the rock stratum it might have been absorbed by a more porous rock, or caused by pressure of water to flow off through sand-rocks of more open texture. The movement of the oil through the rock, displaced from the interstices in which it had originally collected, would have been accelerated as the transition from solid organic tissues to liquid oil had become advanced.

Water, if present in a rock of fine texture, could not by the action of capillarity alone be drawn upward so as to collect in liquid form in a cavity. The same statement is true of petroleum. But the presence of moisture in the interstices of a rock in which petroleum is being generated or in which it is stored in minute pores or spaces might lead to a gradual accumulation of oil from the bulk of the rock into relatively larger spaces such as the cavities of fossils.

Jaccard (*Le Petrole*, 1895, p. 134) has described the occurrence of bitumen in the cavities of fossil mollusks in the Val de Travers in the Jura mountains. Such cases might be regarded as representing a later stage in a series of changes, the original liquid petroleum having passed into solid bitumen long after it was accumulated in

cavities, where its solid condition would tend to its permanent preservation.

The sedimentary limestones contain frequently crystalline calcite cementing together the grains of amorphous mineral matter. Changes in temperature, causing unequal expansion of this calcite in different directions, by reason of the form of its crystals, might in the course of time modify the process by changing the internal structure of the rock. The presence of salt in solution and the solvent action of carbonic acid would no doubt exert an important influence, although its nature could not be foreseen.

The occurrence of petroleum in the fossil shells of mollusks and in the cells of corals would then have no more geological significance than its occurrence in geodes, or in cavities in rocks, or the presence of solid bitumen in hollow quartz crystals or in sphalerite, as all such cases are perhaps attributable to one and the same source, namely, to its presence formerly in a state of wide distribution in the pores of the rock.

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## ON THE COMPOSITION OF AMERICAN PETROLEUM.

BY CHARLES F. MABERY.

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Petroleum is found in Pennsylvania in sandstones of various formations; in southern Ohio in the Berea grit and other sands; in Ohio in the Trenton limestone; in Canada in the Corniferous sandstone; in California, Texas, Colorado, and other American fields in shales and sandstone formations, which represent in general the geological strata in which are the various oil fields in Russia, Roumania, Germany and Austria, Japan, India, etc. Crude oils show great variation in their physical properties, such as color, specific gravity and odor, and differences in their chemical reactions depending on variation in composition.

The first systematic investigation for the purpose of ascertaining the composition of American petroleum was made by Pelouze and Cahours, who referred the entire body of crude oil, including paraffine, to the series homologous with marsh gas,  $C_nH_{2n+2}$ . At about the same time, 1862, C. M. Warren began a study of Pennsylvania